# ORGANIC AND BIOLOGICAL CHEMISTRY

## Iodine and Styrene. I. Four Reactions between Iodine and Styrene

BY DANIEL S. TRIFAN[1] AND PAUL D. BARTLETT

Iodine strongly inhibits the polymerization of styrene by the free radical mechanism. At the same time equilibrium is established rapidly in the dark, at and below room temperature, with styrene diiodide, the equilibrium lying on the side of styrene and iodine. Other products of the combination of styrene and iodine are formed slowly in the dark and much more rapidly in the light. One of these, identified as 1,4-diiodo-2,3-diphenylbutane, has been isolated in 6.3% yield. The disappearance of iodine from its solutions in styrene is greatly accelerated by the presence of oxygen, the product being bis-$\beta$-iodo-$\alpha$-phenylethyl peroxide. Solutions of iodine in styrene more concentrated than 20% bring about, at room temperature, an exothermic polymerization of styrene which is shown to proceed by a cationic mechanism. From a mixture of styrene and methyl methacrylate only polystyrene is produced.

## Introduction

The four reactions to be discussed are the rapid, reversible formation of styrene diiodide, the slow formation of higher iodine–styrene products, the intervention of oxygen to yield a bis-phenyliodoethyl peroxide, and a cationic polymerization of styrene. These will be discussed in that order.

1. **The Reversible Formation of Styrene Diiodide.**—Styrene diiodide was first described by Berthelot.[2] It can be isolated as colorless needles by chilling a 10% solution of iodine in styrene to 0° then making a rapid filtration. It is, however, very unstable, and any attempt to handle it at room temperature results in its decomposition after a few seconds to a dark, sticky mass containing iodine and polystyrene of low molecular weight (see Section 4). The iodine content of styrene diiodide was determined by washing rapidly with ether and adding portions of the freshly washed crystals to tared flasks containing reagent benzene. These samples were titrated with 0.1 $N$ sodium thiosulfate, showing an iodine content of 68.2 and 68.4% (calculated for dry styrene diiodide 70.9%). In a sample which was allowed to decompose in a tared flask without solvent, 12.65% of the iodine became bound in a non-titratable form in the decomposition product.

The iodine color appears instantly on solution of styrene diiodide in styrene or benzene at room temperature; the establishment of equilibrium in the iodine addition-elimination reaction occurs too fast for rate measurements using ordinary techniques.[3]

In addition to the colorless styrene diiodide, there is a complex between styrene and iodine whose presence is evident from the color of the solution. Solutions of iodine in styrene appear to the eye a wine-red color, intermediate between the violet of solutions in benzene and the more nearly brown color of solutions in alcohol. Indeed, the spectrum of a solution of iodine in styrene at 25° can be closely imitated over the range from 440 to 700 m$\mu$ by the use of a mixed solvent containing 94.8% benzene and 5.2% ethanol by volume (see Figs. 1 and 2).

At 100° the color is more violet, corresponding to the charge-transfer complex being formed with some evolution of heat. The optical densities at 25° of solutions of equal concentrations of iodine in benzene–alcohol and in styrene of similar spectrum are in the ratio of 10 to 9, showing that the equilibrium is quite unfavorable to styrene diiodide.

A small but definitely reproducible shift in the position of equilibrium occurs on illumination of the solution. Large effects of this sort have been observed by Forbes and Nelson,[4] who were able to shift the equilibrium in alkylene diiodide formation largely in the one direction or the other by suitable choice of wave length of irradiating light. In general such effects arise from the microscopic irreversibility of the light absorption process, and may be observed whenever a rate constant which is specifically affected by light (in this case the rate constant for the dissociation $I_2 \rightarrow 2I\cdot$) enters into the expression for the position of the over-all dynamic equilibrium.

Three sets of simple experiments on this effect were carried out with a Coleman junior spectrophotometer. Solutions of iodine in styrene, equilibrated in the dark, were suddenly illuminated and the small drop in absorbancy observed. Interruption of the light restored the initial iodine concentration and the cycle could be repeated at intervals of about 20 seconds. The experiments were carried out in a dark room, using iodine concentrations less than 0.000735 $M$ in pure styrene, to which hydroquinone had been added to retard the otherwise rapid reaction of iodine, styrene and oxygen (see Section 3). Table I summarizes the results of a series of such experiments. In each series the successive entries in the table represent repetitions of the cycle with the same sample. Controls of two types are available in testing for the reality of these small shifts in optical density. Table II shows the degree of constancy of the absorbancy observed in an identical set of experiments in which the iodine was dissolved in benzene or in ethanol instead of in styrene. Increases in the transmission of the order of 1% were consistently observed in the styrene experiments and constancy within $\pm0.1\%$ was general in the experiments in

(1) From Part I of the Ph.D. thesis of Daniel S. Trifan, Harvard University, August, 1948. Present address: Plastics Laboratory, Princeton University, Princeton, N. J., where a further part of this work was carried out.

(2) M. Berthelot, *Bull. soc. chim. France*, [2] **6**, 294 (1866).

(3) See part II, THIS JOURNAL, **81**, 5582 (1959).

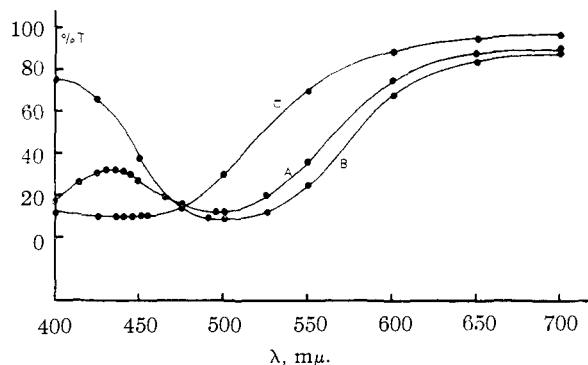(4) G. S. Forbes and A. F. Nelson, *ibid.*, **58**, 182 (1936); **59**, 693 (1937).

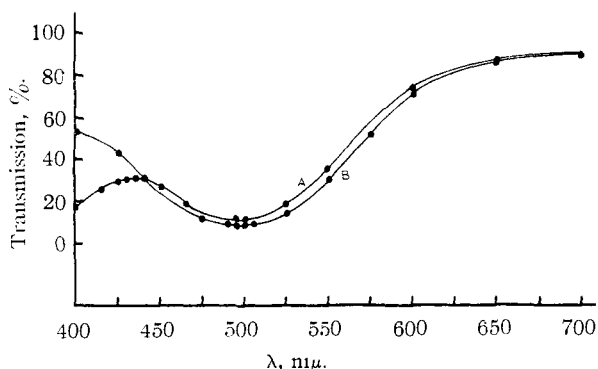Fig. 1.—Spectrum of iodine (7.35 × 10⁻⁴ M) in styrene (A), benzene (B) and ethanol (C).



Fig. 2.—Spectrum of iodine (7.35 × 10⁻⁴ M) in styrene (A), and in a mixture (B) consisting of 94.8% benzene and 5.2% ethanol by volume.

benzene or alcohol solvent. Separate experiments showed that the hydroquinone and iodine did not react under the conditions of the experiments.

TABLE I

INCREASES IN LIGHT TRANSMISSION ON SUDDEN ILLUMINATION OF SOLUTIONS OF IODINE IN STYRENE AT ROOM TEMPERATURE

| Wave length, mμ | Initial % of transmission | Approx. time to reach new constant % transmission, sec. | Shift in % transmission |
|---|---|---|---|
| 500 | 15.5 | 20 | +0.8 |
| | 15.0 | 20 | +1.4 |
| | 15.3 | 20 | +1.2 |
| | 18.0 | 20 | +0.7 |
| | 17.0 | 30 | +1.2 |
| | 43.0 | 15 | +1.5 |
| | 42.9 | 20 | +2.0 |
| | 42.0 | 15 | +2.8 |
| | 48.0 | 20 | +1.0 |
| | 48.0 | 30 | +1.6 |
| | 48.4 | 25 | +1.2 |
| | 48.4 | 20 | +0.9 |

Finally, a type of experiment was carried out in which the direction of the narrow cylindical light beam through the Coleman cell was changed periodically by rotating the cell 90° in its seat, thereby sending the beam through parts of the solution which were formerly dark. On each such rotation the first reading corresponded to a lower transmission which quickly adjusted itself to the higher transmission characteristic of the steady

illuminated state. These experiments, carried out at 550 mμ, are summarized in Table III.

TABLE II

CONSTANCY OF TRANSMISSION OF 0.000735 M SOLUTION OF IODINE IN BENZENE AND IN ALCOHOL

| Solvent | Wave length, mμ | Initial % transmission | Observation period, sec. | Shift in % transmission |
|---|---|---|---|---|
| Benzene | 500 | 8.8 | 60 | 0.0 |
| | | 8.8 | 120 | .0 |
| | | 8.8 | 180 | ± .1 |
| | 550 | 25.5 | 60 | .0 |
| | | 25.3 | 60 | .0 |
| Ethanol | 500 | 29.4 | 60 | ± .1 |
| | | 29.4 | 60 | ± .1 |
| | | 29.3 | 60 | ± .2 |

The significance of this small but definite shift in composition of the reaction mixture with illumination is that the step or steps accelerated by light must enter into the expression for the over-all steady-state concentrations of reactants and product. This fact is incompatible with certain otherwise plausible mechanisms, as will be shown in Part II.

**2. The Slow, Irreversible Disappearance of Iodine. The Photochemical Reaction.**—It was noticed during the experiments of Tables I and III that over a period long compared to the duration of the experiments there was a slow and steady fading of the iodine color on prolonged exposure to light. In bright sunlight an approximately tenth molar solution of iodine in styrene was bleached in 18 hours of exposure. Removal of the styrene by distillation in an all-glass evacuated apparatus into a Dry Ice-cooled receiver left a residue of 5.52 g. of mixed colorless crystals and light brown viscous liquid from an original 2.76 g. of iodine. The calculated yield of diiodo-dimer is 5.04 g., of diiodo-trimer, 6.17 g. These products could be separated only with considerable losses; it was possible to isolate 0.320 g. of 1,4-diiodo-2,3-diphenylbutane (I), m.p. 199.0–199.5° (cor.) This compound was dehydrohalogenated readily to 2,3-diphenyl-1,3-butadiene (II), crude m.p. 37–43°, which was brominated in high yield to the known 1,4-dibromo-2,3-diphenylbutene-2 (III), m.p. 147–148° (cor.), lit.[5] 145–147°.

Attempts to characterize the diiodide by the formation of a bis-trimethylammonium or dimethylsulfonium salt were unsuccessful, leading to the isolation of trimethylammonium iodide and trimethylsulfonium iodide, respectively. The isolation of the tertiary sulfonium salt through easy methylation of dimethyl sulfide by the sought-for sulfonium ion recalls the similar experience of Ray and Levine[6] with dimethyl sulfide and phenyl-2-fluorylbromomethane.

**The Thermal Reaction.**—Even in the dark at room temperature, the decline in color of degassed solutions of iodine in styrene becomes appreciable after about 24 hours. At 100° complete reaction of the iodine is evident after a few hours. At both temperatures the reaction exhibits a remarkable

(5) C. F. H. Allen, C. G. Eliot and A. Bell, Can. J. Research, 17B, 75 (1939).

(6) F. E. Ray and I. Levine, J. Org. Chem., 2, 267 (1937).

TABLE III

EFFECT OF ROTATION OF COLEMAN CELL ON LIGHT TRANSMISSION BY SOLUTION OF IODINE IN STYRENE AT ROOM TEMPERATURE, $\lambda$ = 550 m$\mu$

| Rotation no. | 1 | 2 | 3 | 4 | 5 | 6 | 7[a] | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| % trans., steady | 44.8 | 44.8 | 45.3 | 45.3 | 45.4 | 45.3 | 47.2 | 47.0 | 46.7 | 46.7 |
| % trans. after 90° rotation of tube | 43.3 | 43.7 | 44.0 | 44.0 | 44.0 | 44.4 | 45.5 | 45.5 | 45.3 | 45.8 |
| Shift, % trans. | −1.5 | −1.1 | −1.3 | −1.3 | −1.4 | −0.9 | −1.7 | −1.5 | −1.4 | −0.9 |
| Time (sec.) for drop in % trans. | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 7 | 5 |
| Time (sec.) for return to max. | 20 | ... | 20 | 20 | 20 | 25 | 20 | 25 | 25 | ... |
| New const. max. % transmission | 44.8 | ... | 45.2 | 45.2 | 45.3 | 45.9 | 47.2 | 46.7 | 46.3 | ... |

[a] Between rotation 6 and 7 the tube was removed from the instrument.

autocatalytic character such that the more concentrated the initial solution of iodine, the shorter the time required for complete disappearance of the iodine color. This is a characteristic of reactions whose product is a catalyst for the reaction, and it was found that a completely reacted solution of 0.217 $M$ iodine in styrene served to catalyze the reaction of another such solution, shortening the time to complete disappearance of the iodine color at 100° from 1.3 hours to half an hour. Nevertheless, it did not appear to be the identified product, 1,4-diiodo-2,3-diphenylbutane, which was responsible for this autocatalysis. Two solutions of 0.109 $M$ iodine in styrene, one of which was made 0.0073 $M$ in the diiodo compound, reacted at identical rates.

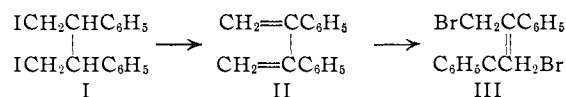Table IV illustrates the results of these experiments.

ICH₂CHC₆H₅     CH₂=CC₆H₅     BrCH₂CC₆H₅
|→       |→
ICH₂CHC₆H₅     CH₂=CC₆H₅     C₆H₅CCH₂Br
   I            II          III

TABLE IV

THERMAL DISAPPEARANCE OF IODINE AT 100° FROM DEGASSED SOLUTIONS IN STYRENE

| Sample | Concn. of iodine, $M$ | Approximate total reaction time, hr. | Special conditions |
|---|---|---|---|
| 1 | 0.434 | 0.5–0.7 | |
| 2 | .434 | 0.25–0.33 | HI[a] |
| 3 | .217 | 1.1–1.4 | |
| 4 | .109 | 2.6–2.7 | |
| 5 | .109 | 1.4–1.6 | HI[a] |

[a] 0.213 g. of concentrated aqueous hydriodic acid (50%) was degassed with 10 ml. of styrene, sealed off, and the tubes shaken vigorously. The concentration of HI in the styrene phase was unknown.

For reasons mentioned below it was suspected that hydrogen iodide might be the autocatalyst in these experiments. The comparison of samples 1 and 2, and of samples 4 and 5, shows that even in the presence of water, which must keep most of the hydrogen iodide out of the styrene phase, there is a substantial catalysis. In samples 2 and 5 final titration showed that 18.1 and 12.5%, respectively, of the acid introduced remained at the end of the reactions. In some control runs with hydriodic acid but without iodine, 29.2 and 27.9% of the acid remained after 1- and 2-hour heating periods at 100°, respectively. It is very unlikely that the degassing procedure removed so much of the acid.

**3. The Reaction of Iodine and Oxygen with Styrene. Structure of the Product.**—If a solution of iodine in styrene is allowed to stand in an open test-tube for a day, a color gradation can be observed along the length of the tube, from the usual dark wine-red at the bottom to a colorless zone at the top. Moureu and Dufraisse[7] reported that iodine and many iodine compounds are catalysts in the autoxidation of styrene. Table V shows the molar ratios of iodine, styrene and oxygen consumed in a series of experiments in which oxygen at one atmosphere initial pressure was absorbed in styrene–iodine solutions until the iodine color was replaced by a very pale yellow amber. In this series of experiments the styrene concentration was varied over a sixfold range in dry benzene as solvent, and the iodine was varied over a sevenfold range in styrene as solvent. The oxygen absorbed was determined both manometrically and gravimetrically and the styrene by titration with bromate–bromide solutions, a process not interfered with by the reaction product.
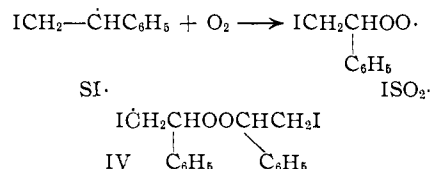
TABLE V

PROPORTIONS OF STYRENE, IODINE AND OXYGEN CONSUMED IN DIFFUSE LIGHT

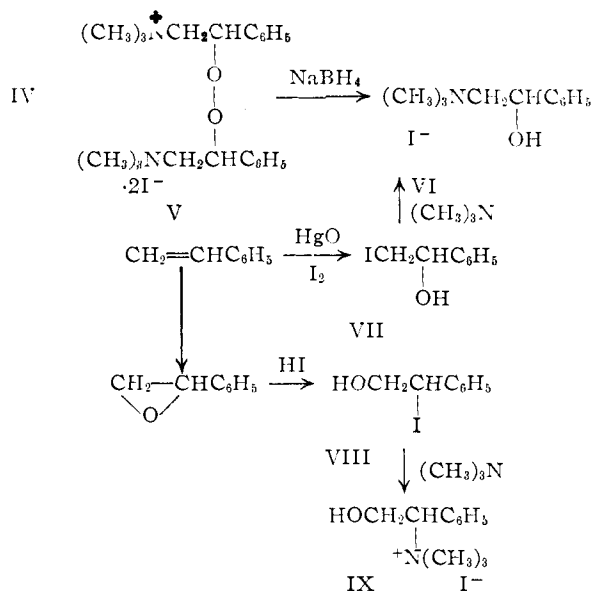| Initial iodine concn., molal | Initial styrene concn., molal | Molar reaction ratio for 100% reaction | | | |
|---|---|---|---|---|---|
| | | Styrene | Iodine | Gravimetric | Manometric |
| 0.2273 | 9.0484 | 2.193 | 1.000 | 1.053 | 1.049 |
| .2311 | 4.5967[a] | 2.419 | 1.000 | 0.999 | ... |
| .2320 | 2.4571[a] | 2.336 | 1.000 | 0.832 | 0.804 |
| .2330 | 1.4843[a] | 2.566 | 1.000 | 1.218 | ... |
| .4301 | 8.5539 | 2.474 | 1.000 | 0.717 | ... |
| .2274 | 9.0489 | 2.150 | 1.000 | .823 | ... |
| .1179 | 9.3150 | 2.157 | 1.000 | .959 | 1.011 |
| .0598 | 9.4567 | 1.866 | 1.000 | .792 | 0.814 |

[a] Dry reagent benzene used as solvent.

It is seen that the product contains styrene, iodine and oxygen in the molar proportions of 2:1:1 with deviations up to 0.566 mole (excess) in styrene and up to 0.283 mole (deficiency) in oxygen. This is consistent with the formation of a peroxidic product, bis-$\beta$-iodo-$\alpha$-phenylethyl peroxide (IV), by intervention of oxygen which attacks the $\beta$-iodo-$\alpha$-phenylethyl radical (SI·) in competition with iodine.

ICH₂—CHC₆H₅ + O₂ ⟶ ICH₂CHOO·
                           |
                           C₆H₅
SI·                      ISO₂·

ICH₂CHOOCHCH₂I
IV   C₆H₅     C₆H₅

The product was characterized by conversion into a bis-trimethylammonium iodide (V), m.p.

(7) C. Moureu and C. Dufraisse, Chemistry & Industry, 47, 819 (1928).

198–199°, in 91% yield, and into the corresponding bis-triethylammonium salt, m.p. 154.0–156.5°. The bis-trimethylammonium salt was reduced with sodium borohydride to 2-hydroxy-2-phenethyl-trimethylammonium iodide (VI), m.p. 226.4–227°, identical by infrared spectrum (Nujol mull) and mixed melting point with the synthetic salt from the iodohydrin VII made by the action of iodine and yellow mercuric oxide on styrene,[8] and different from the salt IX, m.p. 98.5–100°, from the iodohydrin VIII made from HI and styrene oxide.

$$(CH_3)_3\overset{+}{N}CH_2CHC_6H_5$$

IV

$$(CH_3)_3\overset{+}{N}CH_2CHC_6H_5$$
·2I⁻
V

$$\xrightarrow{NaBH_4} (CH_3)_3NCH_2CHC_6H_5 \quad I^- \quad OH$$

VI
(CH₃)₃N

$$CH_2=CHC_6H_5 \xrightarrow[I_2]{HgO} ICH_2CHC_6H_5 \quad OH$$

VII

$$CH_2\!-\!CHC_6H_5 \xrightarrow{HI} HOCH_2CHC_6H_5 \quad O \qquad\qquad I$$

VIII  (CH₃)₃N

$$HOCH_2CHC_6H_5 \quad \overset{+}{N}(CH_3)_3$$
IX   I⁻

The course of this reaction is similar to that observed by Bockemüller and Pfeuffer in the reaction of a number of olefins with bromine and oxygen,[9] but the 2:1:1 ratios maintained in the iodine system over a range of reactant concentrations were not observed in the bromine system, where chain propagation with bromine is far less reversible (see Discussion below).

**Effect of Light, Oxygen and Temperature on Bleaching Rate.**—Like the reaction in the absence of oxygen, the styrene–iodine–oxygen reaction is strongly promoted by light. Both with and without strong illumination the decolorization is more rapid in the presence of oxygen than without it. A 0.109 $M$ solution of iodine in styrene, mounted in a shaker in diffuse laboratory light at room temperature in a slow stream of oxygen, required 20.5 hours for decolorization; in bright sunlight the time was reduced to 0.17 hour. At 100° in dim light, the corresponding times were 2.5–3 and 0.25 hours, respectively. In bright sunlight two 0.109 $M$ solutions of iodine in styrene were compared at 0°, one with and one without saturation with oxygen at one atmosphere. This hundredfold *acceleration* of a chain-terminating process by oxygen, under conditions where the iodination of styrene is already at equilibrium, stands in apparent contrast to the equally great *retardation* by oxygen of the styrene–iodine addition reaction itself (see Part II). The cause of each is the same;

accelerated termination shortens the kinetic chains and therefore lowers the over-all rate of formation of styrene diiodide under non-equilibrium conditions.

The degassed solution required 18 hours for complete reaction, compared to 0.17 hour for the oxygen-saturated solution.

On sudden exposure of a flask containing the vapor of styrene, iodine and oxygen to bright sunlight, a white mist was formed immediately and became quite dense within five seconds, corresponding to the occurrence of the reaction in the vapor phase.

**Retardation by Antioxidants.**—The addition of hydroquinone (excess, in suspension in the solution) caused a period of retardation during which shiny black crystals of quinhydrone could be seen to grow on the hydroquinone crystals. On consumption of the hydroquinone the absorption of oxygen and disappearance of iodine color proceeded at the normal rate. The antioxidant 2,6-di-$t$-butyl-$p$-cresol (Ionol DBPC), being soluble in the reaction mixture, was a still more effective retarder. Table VI shows the results of a series of experiments in each of which 10 ml. of an iodine solution in styrene was shaken with air in a closed 250-ml. erlenmeyer flask which contained 4 moles of oxygen per mole of iodine present.

TABLE VI

RETARDATION BY HYDROQUINONE AND BY 2,6-DI-$t$-BUTYL-$p$-CRESOL (IONOL, DBPC) OF THE IODOPEROXIDATION OF STYRENE AT ROOM TEMPERATURE

| Retarder | Conditions | Time (hr.) to disappearance of iodine color |
|---|---|---|
| | Initial [I₂] = 0.056 $M$ | |
| None | Light[a] | 0.9 |
| None | Dark | 34 |
| Hydroquinone[b] | Light[a] | 17 |
| 0.336 $M$ Ionol (DBPC) | Light[a] | 50 |
| .056 $M$ Ionol (DBPC) | Light[a] | 29 |
| .0055 $M$ Ionol (DBPC) | Light[a] | 5 ± 1 |

[a] Three 40-w. "daylight" fluorescent lamps at a distance of 36″ from the solution. [b] Two moles of hydroquinone per mole of iodine suspended in styrene–iodine solution.

These results are of unusual interest for their bearing on current theories of the inhibition process in autoxidation. In the autoxidation of cumene, Hammond and co-workers[10] obtained important evidence that (1) there is no hydrogen atom transfer in the rate-determining step of inhibition by an antioxidant, (2) there is electron transfer apparently as part of a reversible complex formation between antioxidant and peroxy radical and (3) kinetically the termination of chains involves an inhibitor molecule and two peroxy radicals, clearly indicating that the initial complex formation is reversible. On the other hand, in the classical work of Ziegler on the reaction of oxygen with hexaphenylethane,[11] rate and product studies showed that the effect of pyrogallol on the triphenylmethylperoxy radical was to donate a hydrogen atom, and in so doing to change the product of the reaction from bis-

(8) C. Golumbic and D. L. Cottle, THIS JOURNAL, 61, 996 (1939).
(9) W. Bockemüller and L. Pfeuffer, Ann., 537, 178 (1939).
(10) G. S. Hammond, C. E. Boozer, C. E. Hamilton and J. N. Sen, THIS JOURNAL, 77, 3238 (1955).
(11) K. Ziegler and L. Ewald, Ann., 504, 162 (1933); K. Ziegler, L. Ewald and A. Seib, Ann., 504, 182 (1933).

triphenylmethyl peroxide to triphenylmethyl hydroperoxide.

In an important respect the present autoxidation resembles that of hexaphenylethane rather than that of cumene: the product isolated can arise only in the chain terminating step, and not in chain propagation. If the antioxidants were acting by hydrogen atom transfer to the peroxy radicals, it would be unexpected that this should retard consumption of iodine and oxygen, and it would be impossible that the same product should be formed as in the unretarded oxidation. Every radical stopped by the hydrogen-transfer mechanism should be converted to $\beta$-iodo-$\alpha$-phenethylhydroperoxide, $ICH_2CH(C_6H_5)OOH$, and not to IV at all. This point was therefore investigated carefully. A peroxidation in the presence of three moles of 2,6-di-$t$-butyl-$p$-cresol per mole of iodine was worked up, as soon as the iodine color had become very pale, by reaction with trimethylamine as before. The bis-quaternary ammonium salt was isolated in 65.5% yield and shown by melting point, mixed melting point and infrared spectrum to be identical with the product from the unretarded reactions. No hydroperoxide was isolated, although there was weak O–H absorption in the infrared spectrum of the crude salt. This absorption was shown not to be due to the retarder, since stronger bands of this phenol were absent. These experiments constitute a clear case of retardation, by a factor of the order of 30, of the formation of a chain-termination product without the bulk of the reaction being diverted from its ordinary course by the retarder.

**The Diiodo-Peroxide as an Initiator.**—If the 2:1:1 product is indeed a peroxide, it might be expected to induce further reaction in the styrene-oxygen mixture after the iodine is consumed.[12] At the point of disappearance of iodine color dilution of a 0.109 $M$ solution of iodine in styrene, illuminated in the presence of oxygen, by adding methanol produced only negligible cloudiness. The same was true of a control experiment in which oxygen was bubbled through styrene with high speed stirring in bright sunlight for 1.5 hours at 0°, followed by dilution with 10 volumes of ligroin. However, continued irradiation of the reacted iodine–oxygen solution at 0° for 1.5 hours afforded 2.69% of polymer insoluble in ligroin and in methanol, and 0.31% of such a product resulted from warming an identical solution at 40–45° for two hours. The analysis of the polymeric material formed in the light showed it to be a styrene-oxygen copolymer containing 3.06% of iodine. Assuming two iodine-containing end groups per molecule, this figure corresponds to a styrene-oxygen copolymer of molecular weight 8300 and degree of polymerization about 57. This gummy polymer underwent slow decomposition at 100° with liberation of iodine, benzaldehyde and formaldehyde, the last two identified by their 2,4-dinitrophenylhydrazones as well as detected by their odors.

**4. Cationic Polymerization of Styrene by Iodine. Dependence on Iodine Concentration.**—The

(12) A. A. Miller and F. R. Mayo, THIS JOURNAL, **78**, 1017 (1956).

addition of even a small amount of crystalline iodine to styrene without agitation produces local heating. If the amount of iodine is sufficient (about 20% or more) the reaction becomes violent and the temperature rises rapidly to the boiling point of styrene with prolonged evolution of clouds of iodine vapor and considerable splattering. The iodine color can be removed from the viscous reaction product by triturating with portions of ethanol. On dilution with benzene and stirring into excess methanol a thick layer of polymer precipitates from solution. Polymerization of olefins by iodine has been observed by Berthelot,[13] Moureu and Dufraisse,[7] Staudinger and Bruson,[14] Stobbe,[15] and Wislicenus,[16] and the iodine polymerization of vinyl ethers has been carefully investigated.[17,18] Bartlett and Kwart[19] commented on the dual behavior of iodine toward vinyl acetate—a strong inhibitor, as with styrene, at high dilution, and a strong catalyst for polymerization at moderate concentrations.

In contrast to the 20% (about 0.8 $M$) solutions of iodine, a 0.434 $M$ solution showed no temperature rise on long standing. An increase in viscosity was observable after five days, and by the end of 34 days the solution flowed only very slowly. During the same period of time, iodine solutions of 0.217 and 0.109 molar concentration remained completely fluid. These experiments show that the iodine polymerization of styrene is of order greater than one in iodine. It is also clear from the inhibitory power of iodine for polymerization by free radical mechanisms that this polymerization must be of non-radical and presumably of ionic character.

**Copolymerization Test for Mechanistic Type.**—Copolymerization affords a clear way of distinguishing between free radical and ionic polymerization. Styrene and methyl methacrylate, in a mixture containing similar molar amounts, form a copolymer containing nearly equal amounts of the two monomer units when the polymerization is carried out by a free radical mechanism. Stannic chloride, however, polymerizes styrene by a cationic mechanism to the virtual exclusion of any methacrylate that may be present.[20] A 0.789 $M$ solution of iodine in a mixed solvent of equal volumes of styrene and methyl methacrylate was degassed and allowed to polymerize for several days at about 30°. A white powdery polymer amounting to 31% of the whole was isolated by precipitation with methanol. The analysis of a reprecipitated sample showed 80.83% carbon, 6.56% hydrogen and 12.62% iodine, accounting for 100.01% of its weight. Polymerization of such a mixture by any free radical mechanism would have yielded a copolymer containing an estimated 13.7% of

(13) M. Berthelot, *Bull. soc. chim. France*, [2] **7**, 277 (1867).

(14) H. Staudinger and H. Bruson. *Ann.*, **447**, 110 (1926).

(15) H. Stobbe and K. Toepfer, *Ber.*, **57**, 489 (1924); H. Stobbe, *ibid.*, **45**, 3403 (1912).

(16) J. Wislicenus, *Ann.*, **192**, 113 (1878).

(17) W. Chalmers, *Can. J. Research*, **7**, 472 (1932).

(18) D. D. Eley and A. W. Richards, *Trans. Faraday Soc.*, **45**, 425 (1949).

(19) P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1056 (1950).

(20) C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, *ibid.*, **72**, 48 (1950); F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 278 (1950).

oxygen, allowing for the same iodine content and the proportions of monomer units indicated by the work of Mayo and Lewis.[21] It is clear, therefore, that the iodine in acting as a polymerization catalyst must be doing so through the production of cations from the styrene, since in anionic polymerization, methacrylate is more reactive than styrene, not less.

## Initiation and Termination Mechanisms,—The

high order of this polymerization with respect to iodine is to be correlated with the observations of Robertson and others[22] that the polar addition of halogens to the carbon–carbon double bond becomes of high order in the halogen when the solvent has a low solvating power for anions. Thus instead of the initiating step (1) the increased electro-

$$(1) \quad X_2 + \diagdown C{=}C\diagup \longrightarrow \left[ \diagdown C \diagdown C \diagup \atop X \right]^{+} + X^{-}$$
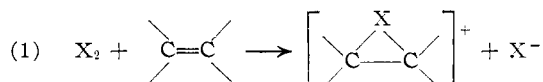
static potential of the negative ion in non-polar solvents requires the formation of the ions of less concentrated charge, $X_3^-$ and $X_5^-$, in the rate-determining step of the initiation, with consequent increase in the order with respect to halogen.

A cryoscopic determination in benzene yielded a value of 1400 for the molecular weight of the polystyrene isolated from the mixture of styrene and methyl methacrylate. On the basis of one iodine atom per polymer molecule, the iodine content would afford an estimated molecular weight of 1006, a result in close agreement with viscosity data, using the equation of Kemp and Peters. The cryoscopic result would indicate that 39% of the polymer chains are terminated by combination of the polystyrene cation with iodide ion, and 61% by loss of a proton to produce a terminal double bond.

Iodine-induced ionic polymerization of styrene is obviously involved in the decomposition of solid styrene diiodide described in Section 1, since the solution of iodine in styrene which results from the dissociation of styrene diiodide is far above the critical value for uncontrolled exothermic polymerization. The close coincidence of the iodine consumed in the decomposition of styrene diiodide without solvent and the iodine content of the isolated polymer is probably fortuitous.

## Discussion

The equilibrium formation of styrene diiodide in the dark at low temperatures occurs too rapidly to be initiated by the simple dissociation of iodine into iodine atoms.[3] This leaves the question open whether the reaction is in fact of radical or ionic character. The other three reactions of the styrene–iodine system, described here, show that at room temperature, in styrene or other organic solvents, both free radical and ionic processes are occurring fast enought to contribute to the attainment of addition–elimination equilibrium. This conclusion is supported by other evidence to be developed in Part II,[3] where it is shown that over 99% of the formation of diiodide at room temperature is

inhibitable and therefore a chain reaction, but that a reaction still remains which cannot be inhibited. This reaction may well be ionic, but it is still much faster than the ionic polymerization.

These facts are consistent with the occurrence of a very low steady-state concentration of $\beta$-iodo-$\alpha$-phenylethyl radicals (SI·), their concentration being kept low by the high rate of the chain-carrying reaction

$$\underset{C_6H_5}{ICH_2CH\cdot} + I_2 \rightleftharpoons \underset{C_6H_5}{ICH_2CHI} + I\cdot$$
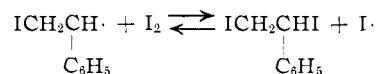
Both the formation of diiodo-dimer and that of diiodo-peroxide can be accounted for simply as a slow coupling and interception by oxygen, respectively, of the $\beta$-iodo-$\alpha$-phenylethyl radical.

The significance of the photodisplacement in the formation of styrene diiodide will be discussed further in Part II.[3] As remarked in Section 1 above, such a displacement must mean that the rate constant affected by light enters into the determination of the over-all position of the dynamic equilibrium. In a mechanism for iodination of the double bond which is successful in the case of ethylene,[27,24] the only initiating and terminating steps are those of the iodine dissociation equilibrium

$$I_2 \rightleftharpoons 2I\cdot$$
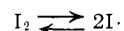
It can be shown by the usual steady-state treatment that a shift to the right in this equilibrium will not affect the relative rates of formation and destruction of styrene diiodide, if this occurs only in *chain propagating* steps. Therefore, either the light used causes several per cent. of the iodine to be converted at the steady state into iodine atoms, or else there is a chain terminating step other than the union of iodine atoms, for example

$$\underset{C_6H_5}{ICH_2CH\cdot} + I\cdot \longrightarrow \underset{C_6H_5}{ICH_2CHI}$$
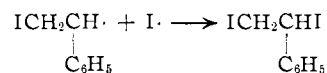
The former alternative can be excluded. If so much as 0.5% of the iodine in $7 \times 10^{-4}$ M solution were to be converted under illumination into iodine atoms, the pseudo-equilibrium constant would be $7 \times 10^{-8}$. Combining this with the measured rate constant of recombination of iodine atoms[25] in the gas phase at 25°, probably of the same order of magnitude as the rate constant in styrene solution, we find that $k_d$ for the photodissociation of iodine would have to be about 500 liters per mole second, an impossibly high value. It follows that there is an important mode of chain termination other than recombination of iodine atoms. Evidence for its nature will be presented in Part II.

Pending further work on the autocatalysis of the irreversible iodine consumption, it seems a reasonable suggestion that the catalyst is hydrogen iodide, formed in the concurrent ionic polymerization. Hydrogen iodide was shown above to catalyze this reaction. It is known to be a catalyst for addition of iodine to the double bond,[26] al-

(21) F. R. Mayo and F. M. Lewis, THIS JOURNAL, **66**, 1594 (1944).

(22) Reviewed by P. B. D. De la Mare, *Quart. Revs.*, **3**, 130 (1949).

(23) M. J. Polissar, THIS JOURNAL, **52**, 956 (1930).

(24) H. J. Schumacher, *ibid.*, **52**, 3132 (1930).

(25) R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 2086 (1953).

(26) H. Berthoud and M. Mosset, *J. chim. phys.*, **33**, 288 (1936).

though the mechanism of the catalysis is not known and we do not know how it would operate here. Hydrogen iodide must accompany every polymer molecule which ends in a double bond rather than in a second iodine being added in anionic form. The higher order of the polymerization with respect to iodine would cause much more catalyst to be produced at higher iodine concentrations. The absence of the autocatalysis in the photochemical reaction would be due to the greater speed of the whole process, affording less time for the light-independent polymerization to occur and build up catalyst. Since a large part of the product from which the 1,4-diiodo-2,3-diphenyl-butane was isolated was non-crystalline and viscous, it is clear that polymerization was an important side reaction.

The observed retardation of the formation of bis-$\beta$-iodo-$\alpha$-phenylethyl peroxide (IV) by hydroquinone and by 2,6-di-t-butyl-$p$-cresol, while the principal product of the retarded oxidation continues to be the same peroxide IV, contributes new evidence on the details of antioxidant action. The three radicals involved in chain propagation are I·, SI· and the peroxy radical $ISO_2$·. If the thirty-fold retardation were brought about by any one of these radicals accepting a hydrogen atom from the retarder, or combining in such a way as to give a derivative of the retarder, the iodine would be more than 96% consumed in the formation of hydrogen iodide, $\beta$-phenethyl iodide, $\beta$-iodo-$\alpha$-phenethyl hydroperoxide or some other product entirely different from the peroxide IV. Actually this peroxide still constitutes the bulk of the iodine-containing product. Only one possibility appears to remain: that the phenolic retarder forms with a chain carrying radical a complex which is reversibly dissociable but much less reactive than the free radical itself.

## Experimental

**Purification of Materials.**—The styrene (Eastman Kodak Co. Grade 1465, stabilized with $t$-butylcatechol) was freed from the stabilizer by distillation through an 18-inch Vigreux column with a spray trap condenser. The distillation was carried out in an all-glass apparatus at the reduced pressure of the water aspirator (11 to 17 mm. pressure) with a potassium hydroxide drying tube in the vacuum line between the aspirator and the distillation apparatus. A boiling capillary was used which was connected to a tank of pre-purified grade nitrogen in order to ensure exclusion of oxygen during the distillation. A 15% forerun and a 20% residue were rejected. Bromate-bromide titration of duplicate samples of the purified styrene usually gave the same result within less than 0.1%. The extremes of 15 analyses on 6 batches were 98.95 and 99.42%. The distilled styrene was stored under pre-purified nitrogen in a stoppered flask in the dark refrigerator and was always used within five to six days of its distillation. To avoid the introduction of atmospheric moisture the stoppered flask of styrene was always allowed to warm to room temperature before being opened.

Reagent grade iodine from Merck and from Mallinckrodt was used without purification after it was determined that the results were the same with and without further purification. The purification procedure consisted of sublimation after trituration with reagent grade potassium iodide and calcium oxide.[27]

The particle size of the iodine crystals was an important consideration in the actual process of preparing solutions in styrene. If the iodine was too finely ground or in the form of

(27) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, p. 622.

very thin platelets, solution was rapid and the critical concentration for producing ionic polymerization was exceeded at the point of contact between the styrene and the crystals. With finely ground iodine the resulting heat evolved was sufficient to produce a hissing sound as the iodine was added to the styrene. Since large crystals dissolved inconveniently slowly and it was desired to minimize the contact with the air, the solutions were eventually prepared from those iodine crystals which passed through holes in a plastic bottle cap 0.063 inch in diameter and which failed to pass holes 0.043 inch in diameter. The iodine crystals were stored in an ungreased desiccator over calcium chloride.

**Measurements of the Concentration Displacement by Light in the Iodine–Styrene Diiodide Equilibrium.**—To provide maximum contrast of light intensity these measurements were made in a dark draft-free room. The spectrometer light source was first allowed to reach constant illumination (about one hour), after which time the galvanometer readings were found to be remarkably steady (see Table II). The data of Table II were taken partly before and partly after the measurements in Table I. Fluctuations in percentage transmission during periods of observation up to three minutes were consistently between 0.0 and 0.1 in the case of benzene and alcohol solvents.

In making the actual measurements the galvanometer setting was adjusted to 100.0% transmission with a blank cell containing solvent. The instrument used throughout this series was the Coleman Junior spectrophotometer which uses cylindrical cells. After adjustment of the dark setting the dark-equilibrated styrene solution was inserted rapidly in the instrument and the fall of the galvanometer needle observed. Four to five seconds was required for the needle to reach its first reading of percentage transmission. This was followed by a steady climb in percentage transmission over the next twenty seconds, at which point the reading became constant and corresponded to the new position of the equilibrium. The value of the shift reported in Table I is the difference between this high and the initial low percentage transmission reading. In the case of the iodine solutions in benzene or in alcohol the galvanometer needle after dropping from 100% remains fixed at the initial reading.

The data presented in Table III were obtained at a later date using a fresh styrene–iodine solution and again employing the precautions described above. However, in this experiment the procedure involved the introduction of the solution into the instrument and allowing time for the shifted equilibrium in the light path to become established. The tube was rotated rapidly 90° about a vertical axis and the drop in the percentage transmission reading noted. This was followed by the usual increase in reading over the next twenty seconds to a value equal to that observed before the rotation. This cycle was repeated many times.

As a control in this type of experiment the identical procedure employing the same absorption cell was repeated with a solution of iodine in benzene. Numerous 90° rotations of the cell in the light path here gave 0.0 or occasionally 0.1 fluctuations in the percentage transmission. Readings remained constant within 0.1% over 2-minute periods of observation.

**Reaction of Trimethylamine with the Product of Fading of Iodine–Styrene Solutions.**—Solutions of iodine and styrene at two concentrations were prepared and degassed in the usual manner. The first solution was prepared by adding 8.257 g. of iodine to 300 ml. of styrene to give a 0.109 molar solution, and the second by adding 16.50 g. of iodine to 3000 ml. of styrene to give a 0.217 molar solution. These solutions were irradiated with three 200-watt lamps while cooled in running tap water. After the reactions were completed the flasks were opened and their contents quantitatively transferred with benzene to erlenmeyer flasks and twice the theoretical amount of trimethylamine in benzene was added to each solution. The resulting solutions remained clear for about one minute, after which time the white insoluble salt formed rapidly in each flask during the next 15 to 60 minutes. No appreciable rise in temperature occurred.

After several days the salt was separated from each solution and washed on a sintered glass funnel with petroleum ether. The dried crystalline solids from the original 0.109 and 0.217 molar solutions weighed 11.854 and 25.344 g., respectively, and corresponded to 97.5 and 100.2% yields based on the initial iodine used and calculated as trimethyl-ammonium iodide. These salts were recrystallized from hot 95% ethanol. Their respective melting points were 257–

261° and 259–263° with decomposition. Authentic trimethylammonium iodide melted at 260–263° with decomposition and mixed melting points of this authentic sample with each of the above salts gave values of 259–263° and 260–263°, respectively.

**Reaction with Dimethyl Sulfide.**—In an identically prepared experiment dimethyl sulfide was used instead of trimethylamine. After ten hours of heating under reflux at 100 to 110°, only half a gram of a white insoluble salt was formed. Refluxing was continued for several more days, after which time the accumulated white salt was separated, washed and weighed. Refluxing for an additional four days yielded a like amount of solid and on the basis that the substance was actually trimethylsulfonium iodide, the combined salt represented a yield of 70.3%. This salt decomposed before its melting point and was identified by an iodine analysis. Calcd. for $(CH_3)_3S^+I^-$: I, 62.19. Found: I, 62.22.

**Isolation of 1,4-Diiodo-2,3-diphenylbutane.**—One hundred milliliters of a 0.109 molar solution of iodine in styrene was degassed in a tube of 25-ml. diameter and kept frozen in Dry Ice at all times except when irradiated with direct bright sunlight. During the 18 hours of irradiation required for the complete reaction of the free iodine the solution was cooled in an ice–water-bath. The 93.43 g. of decolorized solution was transferred to a one-piece 2-bulb glass apparatus and carefully degassed and sealed off. By cooling the empty bulb in Dry Ice it was possible to distil over the unreacted styrene overnight at room temperature. A mixture of colorless crystals and light brown viscous liquid weighing 5.52 g. altogether remained behind.

The crystals were separated from the residual viscous liquid by diluting the latter with ether and filtering on a sintered glass funnel. Since this procedure involved solubility losses, the yield of 0.320 g. obtained could not be considered quantitative. Neither was it possible to examine further the viscous liquid originally present in the residue since it had a strong tendency to liberate free iodine and undergo conversion into a very viscous dark mass.

The distillate from the original isothermal distillation yielded a positive test for iodine with alcoholic silver nitrate. It was therefore subjected to a further vacuum distillation. It was virtually all styrene, boiling point 46° at 17 mm., but less than 1 ml. of a high boiling liquid remained in the distillation flask and could not be further distilled because of its ready loss of iodine.

Recrystallization of the solid from hot benzene–ligroin yielded crystals melting at 199.0–199.5° (cor.). *Anal.* Calcd. for $C_{16}H_{16}I_2$: C, 41.58; H, 3.49; I, 54.93. Found: C, 41.38; H, 3.71; I, 55.25. When tested in alcohol solution with silver nitrate this substance gave a positive test only after 30 seconds at room temperature. The turbidity then increased steadily for several minutes. On heating of the compound on a spatula in an open flame iodine vapor was evolved.

**Conversion of 1,4-Diiodo-2,3-diphenylbutane to 1,4-Dibromo-2,3-diphenylbutene-2.**—Of the original crude diiodo-diphenylbutane 0.062 g. was heated under reflux with 100 ml. of a $2N$ potassium hydroxide solution in ethanol for one hour and evaporated to about 10 ml. with suction. Dilution with water and several extractions with ether, followed by washing and drying of the ether phase, yielded a crude yellowish solid on evaporation which was not further purified and had a melting range of 37–43°. This impure diphenyldiene was dissolved in a small amount of chloroform and was brominated by dropwise addition of a considerable amount of a chloroform solution of bromine. The solvent was evaporated to dryness by suction and the residue dissolved in about half a milliliter of hot ethanol. On cooling and complete removal of the solvent the dibromide crystallized as white needles in a 0.046 g. yield compared to the 0.049 g. theoretical based on the original starting weight of the diiododiphenylbutane (94% yield). The dibromide melted sharply at 147–148° (cor.), literature[6] 145–147°.

**Determination of the Molar Reaction Ratios of Styrene, Iodine and Oxygen.**—The reactions were carried out in 24/40 250-ml. Florence flasks equipped with stopcock joints. By use of a set of calibrated pipets an exact amount of styrene was pipetted into the flask as well as an additional exact amount of dry reagent benzene in those cases where the monomer concentration was varied. The flasks were briefly flushed with dry oxygen and weighed iodine crystals then rapidly and quantitatively introduced from a small weighing bottle. The stopcock joint coated with vacuum stopcock

lubricant was inserted while the solution was being swirled to dissolve the iodine. After the iodine had dissolved, 1 to 2 minutes, the flask was immersed in a 25.0° thermostat and the stopcock opened and closed. The atmospheric pressure at this time was noted and recorded. The flask was also carefully dried and weighed on the gravimetric balance.

After reaction times of 20 to 50 hours when the iodine had been fully consumed in darkness and diffuse laboratory light, the flask was immersed again in a 25° thermostat and connected through a three-way stopcock to a mercury manometer and to the air through a potassium hydroxide drying tube. The stopcock was opened and the pressure drop noted as well as the atmospheric pressure at that particular time. Since the total volume of the manometric system had been determined, it was possible to calculate the moles of oxygen reacted.

The gravimetric result was obtained by allowing dry air to pass into the flask and restoring the pressure to the prevailing atmospheric pressure. The increase in weight of the flask when properly corrected for the ratio of the weights of oxygen to air, 1.103, and also for the change in atmospheric pressure during the interval of the experiment, gave a gravimetric result for the oxygen reacted which agreed within several per cent. with the manometric result.

The styrene consumed during the reaction was determined by bromimetric analysis and the procedure employed here gave consistent, reproducible results. Styrene analyses were made on the original unreacted monomer as well as on the solution at the end of the reaction, and the styrene reacted was obtained by difference.

A weighing bottle of about 5-ml. capacity was equipped with a ground glass dropper and triplicate samples of 4 to 6 drops (about 0.7 to 0.1 g.) of the styrene monomer or reacted solution were weighed out by difference directly into the 250-ml. bromination flask containing 35 ml. of glacial acetic acid plus 5 ml. of 10% sulfuric acid. The bromination flask was evacuated on the aspirator and 10 ml. of 0.09 molar standard bromate–bromide solution was carefully pipetted out and washed into the bromination flask with several portions of distilled water. Several drops of 3% ammonium molybdate solution were added which perhaps served to speed the release of bromine by several minutes. The triplicate flasks were placed in a dark cupboard for 5 or 10 minutes, after which time the first flask was removed and 35 ml. of distilled water added to lower the acidity of the solution prior to the addition of excess reagent potassium iodide which was washed into the partially evacuated bromination flask with distilled water. After brief swirling the bromination flask was opened and the liberated iodine promptly titrated with 0.05 $N$ thiosulfate. Starch solution was added at the approach to the end–point and it gave a satisfactory color at this dilution in acetic acid. The bromate-bromide solution was restandardized using this same procedure with each set of analyses conducted. Styrene analyses were usually reproducible to one part per thousand employing this procedure.

Oxidation of iodide ion by the bis-β-phenylethyl peroxide proceeded quite slowly and did not interfere in this brimimetric procedure, if the iodine titration was carried out promptly.

**Isolation of the Phenyliodoethyl Peroxide as the Bisquaternary Ammonium Iodide.**—To 150 ml. of styrene in a 1-l. flask, 8.249 g. of iodine was added in four portions with swirling. The flask was flushed with dry oxygen, stoppered and placed near a 100-watt lamp while also in diffuse daylight. The flask was swirled occasionally. By the end of 6 hours all the iodine had reacted. The solution was transferred to a 250-ml. glass stoppered erlenmeyer flask, being rinsed in with benzene. Twice the calculated amount of trimethylamine was added (7.68 g.) in benzene solution to the above flask. The solution set at once with the production of a large amount of finely divided insoluble crystalline salt, accompanied by a rapid rise in temperature to about 45°. After standing overnight the solution was filtered through a sintered glass funnel and washed with numerous portions of petroleum ether. The bis-quaternary ammonium salt amounted to 18.10 g., corresponding to a 91% yield based on the original iodine. After recrystallization from boiling ethanol the salt had a melting point of 198–199° (cor.) with some decomposition. *Anal.* Calcd. for $C_{22}H_{34}$-$N_2I_2O_2$: C, 43.15; H, 5.59; N, 4.58; I, 41.45. Found: C, 43.33; H, 5.42; N, 4.37; I, 41.43.

In the similar reaction with triethylamine the bis-quater-

nary salt formed slowly as an immiscible oil which crystallized overnight. This salt was recrystallized several times from hot ethanol and melted at 154.0 to 156.5° (cor.) with decomposition. *Anal.* Calcd. for $C_{28}H_{48}O_2N_2I_2$: C, 48.28; H, 6.66; I, 36.44; N, 4.02. Found: C, 48.81; H, 6.61; I, 36.60; N, 3.84.

**Structure of the Bis-trimethylammonium Peroxide Salt.**—In preliminary tests, sodium borohydride in water was found to be the best reducing system for isolation of products. Bis-peroxide salt (2.00 g.) was treated with 1.0 g. of sodium borohydride in 70 ml. of water. After 4 hr. at room temperature the solution was heated to boiling for about 1 hr. and then concentrated by evaporation. Several crops of crystals were obtained by successive concentration from which a maximum yield of rather pure material (1.72 g., 86% of theory, m.p. 226–230°) was collected. Recrystallization of these fractions gave pure product of m.p. 226.4–227° in good recovery, together with slightly impure residues, m.p. 223.5–227°.

**Preparation of Reference Samples. (a) 1-Phenyl-hydroxyethyltrimethylammonium Iodide.**—The iodohydrin, 2-iodo-2-phenyl-1-ethanol, was prepared by the procedure of Golumbic and Cottle,[8] from styrene oxide in petroleum ether and concentrated hydriodic acid. The iodohydrin, m.p. 76–77° (lit. 78.5°), gave an instant quantitative precipitate with alcoholic silver nitrate. The trimethylammonium salt was prepared by dissolving 4.5 g. of the iodohydrin in 30 ml. of benzene and adding a solution of 4.84 g. of trimethylamine in 22 ml. of benzene (4-fold excess). Turbidity appeared within 2 minutes and after 24 hours the product was isolated by filtration in 94% yield (5.24 g.) and recrystallized with difficulty from acetone–benzene, m.p. 98.5–100°. The salt is freely soluble in cold ethanol, in contrast to its isomer. *Anal.* Calcd. for $C_{11}H_{18}NIO$: C, 43.01; H, 5.90; N, 4.56; I, 41.32. Found: C, 43.16; H, 5.96; N, 4.66; I, 41.24.

**(b) 2-Phenyl-2-hydroxyethyltrimethylammonium Iodide.**—The isomeric iodohydrin, 2-iodo-1-phenylethanol, was obtained by the reaction of styrene with iodine and freshly prepared yellow HgO in ether.[8] It melted at 34.0–34.5° (lit.[8] 34°) and gave only gradual milkiness with alcoholic silver nitrate. In the identical procedure described above to prepare the trimethylammonium salt, this isomer gave no turbidity for 20 minutes. The yield of quaternary salt was 0.387 g. after 24 hr. and 1.067 g. after 90 hr. The crude product melted over a range from 195 to 230°, and was purified by treatment of the aqueous solution with NaOH, concentrating *in vacuo* to remove trimethylamine, neutralizing with HI, evaporating, and recrystallizing from ethanol. The purified salt melted at 224–227°, alone and when mixed with the salt prepared by reductive cleavage of the peroxidic bis-quaternary ammonium iodide. *Anal.* Calcd. for $C_{11}H_{18}NIO$: C, 43.01; H, 5.90; N, 4.56; I, 41.32. Found: C, 42.91; H, 5.84; N, 4.46; I, 41.06. Admixture of even small proportions of 2-hydroxy-1-phenylethyltrimethylammonium iodide gave substantial melting point depressions. Infrared spectra in Nujol confirmed the identity of samples of 2-hydroxy-2-phenylethyltrimethylammonium iodide from synthesis and from reduction of the peroxide.

The great difference in reactivity toward trimethylamine of the isomeric iodohydrins of styrene is reflected also in the behavior of α- and β-phenylethyl iodides; 5.03 g. of each isomer in 60 ml. of benzene was brought into reaction with 2.64 g. of trimethylamine in 12 ml. of benzene (2-fold excess). The salt from the secondary iodide was formed in a yield of 96% in an hour, m.p. 146–147° after recrystallization. The salt from the primary iodide began to appear within 5 minutes, continued a slow accumulation over several days, and was present in 54.5% yield after 3 days. The product, m.p. 200–220°, was freed from trimethylammonium iodide (m.p. 266–267°) by recrystallization. Its melting point, 233.5–235°, was depressed to 211–214° by mixing with the quaternary iodide produced by reduction of the

peroxide salt. *Anal.* Calcd. for $C_{11}H_{18}NI$: C, 45.37; H, 6.23; N, 4.81; I, 43.59. Found: C, 45.64; H, 6.46; N, 4.99; I, 43.66.

Treatment with $NaBH_4$ produced no change in the characteristic infrared spectrum of 2-hydroxy-1-phenylethyltrimethylammonium iodide.

**Product Isolation from Styrene–$I_2$–$O_2$–DBPC Reaction.**—DBPC (Ionol, 1.476 g., 3-fold excess) was dissolved in 20 ml. of styrene in a 250-ml. g. s. flask and 0.2850 g. of $I_2$ added. The flask was flushed with $O_2$, stoppered and mounted on a shaker using an additional 150 w. light bulb in an aluminum reflector 18″ from the flask. After 8.5 hours the remaining iodine color was only very pale and the contents were promptly treated with 4 ml. (6-fold excess) of triethylamine–benzene solution (0.191 g./ml.). Within one minute turbidity developed and in several minutes significant salt was present and slight heat of reaction evident. After 11 hours, 0.4506 g. of salt was collected, crude m.p. 189–193°. Recrystallization from ethanol–water (and avoiding heat) gave fractions, m.p. 194–197°, in very high recovery. This product proved to be bis-peroxide salt, mixed m.p. with pure bis-peroxide salt, 195–197° (undepressed). Infrared spectra also showed the two substances to be identical. No evidence of any hydroxyl absorption was present in the recrystallized material.

Of some possible interest is the infrared spectrum of the crude original salt which has, in addition to the peroxide peaks, several weak but definite absorption bands which although not attributable to DBPC, $(CH_3)_3N \cdot HI$, 2-hydroxy-2-phenylethyltrimethylammonium iodide or β-phenethyl iodide salt could still be due to an oxidation end-product of DBPC present as impurity. The latter possibility is indicated by the appearance of a yellow impurity in some of the recrystallization fractions.

However, a quite weak but reproducible hydroxy absorption is present in the spectrum of crude salt (unlikely to be due to DBPC impurity since stronger bands are absent) which still suggests the possible presence of some hydroperoxide salt.

The mother liquors from which the above crude salt (65.5% based on bis-peroxide) was separated did not yield noticeable additional salt for 1-2 days. After a total of 11 days, however, *ca.* 0.1 g. further salt is estimated to have formed, but has not been examined.

**Preparation of Degassed Solutions.**—All of the experiments on the iodine–styrene system with the exception of those involving the reactions with oxygen were carried out under degassed conditions. Solutions of desired concentration were prepared by addition of the iodine in portions to styrene in a volumetric flask and making up to the mark at 20°. The solution of the iodine was carried out with as dim laboratory illumination as possible and with the volumetric flask flushed with nitrogen to reduce to a minimum the extent to which the reaction with oxygen might proceed prior to degassing. The flasks or drawn out test-tubes to be used were carefully cleaned and flamed and flushed with nitrogen prior to filling. The degassing was accomplished by alternately freezing, pumping and thawing three or four times and sealing off with a torch on the following freezing step at the maximum vacuum of the Cenco Hyvac pump.

CAMBRIDGE, MASS.
PRINCETON, N. J.